



UV light-activated decomposition/cleaning of concentrated biomass wastes involving also solid suspensions with remarkably high quantum efficiency

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ABSTRACT

UV light-activated decomposition/cleaning of high concentration ($>10^3$ – 10^4 ppm) biomass model and wastes in water involving also solid suspensions into CO₂ and N₂ were achieved by using a specially designed biophotochemical cell (BPCC) comprising a nanoporous semiconductor (TiO₂) film photoanode/an O₂-reducing cathode unit and a large volume bulk aqueous phase with a remarkably high internal quantum efficiency over 80 (=8000%) for pig urine.

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1. Introduction

Photoelectrochemical reactions at semiconductor electrodes were investigated before 1960s [1], and the report on a crystalline *n*-TiO₂ photoanode to photodecompose water by UV light attracted a great deal of attention [2]. Organic compounds have also been photodecomposed by using crystalline TiO₂ photoanodes [3,4]. The *n*-semiconductor forms a kind of Schottky junction at the semiconductor/aqueous electrolyte interface, the photogenerated holes oxidize organic compounds on the semiconductor surface, and the photogenerated electrons reduce protons to produce H₂ at a counter electrode. However, without applied potentials the photoelectrochemical reactions were not efficient enough, so that these reactions have mostly been investigated under applied potential conditions. In the beginning of 1990's, a nanoporous TiO₂ thin film was applied to fabricate a dye-sensitized solar cell (DSSC) operated without any applied potential [5]. In this DSSC the nanoporous TiO₂ film works only in an organic liquid electrolytes solution, while it works as an electron acceptor for the photoexcited dye and at the same time as an electron-conducting material rather than working as a liquid-junction semiconductor. The photoreactivity of a nanoporous semiconductor film having a large area of effective interface is an interesting and important issue towards applications, but the details have not been

investigated well. From the beginning of 1990's powders and coatings of TiO₂ were used to photodecompose and clean environmental pollutants and dirty materials by UV light [6], and they have obtained a market called as photocatalyst. However, the activity of the powder-based photocatalysts has been not high, limited usually to less than 100 ppm order pollutants in water, so it has been difficult to clean a high concentration and a large volume of biomass and organic wastes in water, serious pollutants all over the world.

The reasons for the low activity of conventional semiconductor photocatalysts have been that they need to be loaded on carrier to separate after cleaning, which hinders UV light irradiation on semiconductor and drastically lowers its catalytic activity by the surrounding carrier materials. Therefore, it has been almost impossible to clean concentrated, colored, and/or solid suspended pollutant solution due to the strong absorption of the light by the carrier materials, solutes and/or suspended materials. To our knowledge, quantum efficiency of such conventional photocatalysts exceeding 1 (=100%) has not been reported. In order to increase photocatalyst's activity, narrow bandgap semiconductors capable of using visible light have been developed and achieved some success, but still the activity is not sufficient enough to photodecompose and clean high concentration and a large scale pollutants. Such environmental pollution especially by biomass and organic wastes is becoming more and more a serious issue in our society [7].

The present authors have proposed a biophotochemical cell (BPCC) composed of a nanoporous semiconductor photoanode and

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an O_2 -reducing cathode that can photodecompose biomass and its wastes in water capable of generating simultaneously electrical power [8–11]. In further investigations we have succeeded in remarkably enhancing the efficiency of the BPCC to photodecompose and clean highly concentrated organic compounds and biomass wastes by UV light with very high quantum efficiency [12]. In the following researches we have succeeded in photodecomposing highly concentrated biomass and its wastes involving also solid suspensions, and the results will be reported in this paper.

2. Experimental

2.1. Materials

TiO_2 (P-25) was received from Japan Aerosil Co. Ltd. (particle size ca. 20 nm). Ti-nanoxide T/SP paste was purchased from Solaronics Co. Ltd. F-doped SnO_2 conductive glass (FTO, surface resistance $10 \Omega/\square$) was purchased from AGC Fabritec Co. Ltd.

A nanoporous TiO_2 film was prepared as follows. 12 g TiO_2 (P-25, received from Japan Aerosil Co. Ltd.) and acetylacetone (0.4 mL) were mixed well in a mortar while adding slowly 20 mL water. Triton X-100 (0.2 mL) detergent was added and further mixed well with the TiO_2 slurry, and then the mixture was sonicated for 30 min. This mixture was spin-coated (2000 rpm) on an FTO electrode (coated area was either $4 \text{ cm} \times 4 \text{ cm}$ or $5 \text{ cm} \times 5 \text{ cm}$ on either $5 \text{ cm} \times 5 \text{ cm}$ or $6 \text{ cm} \times 6 \text{ cm}$ size FTO, respectively) for about 10 s to obtain a nanoporous TiO_2 film, and the film was dried at 100°C for 30 min. This procedure was repeated until the film thickness became $10 \mu\text{m}$, and finally the film was calcined at 450°C for 30 min. In another case commercially available Ti-nanoxide T/SP paste was coated on an FTO by a squeeze coating method. For this process, an adhesive tape (thickness about $70 \mu\text{m}$) was used as a spacer to adjust the TiO_2 film thickness to around $10 \mu\text{m}$. The deposited TiO_2 film was dried at room temperature, and then calcined at 450°C for 30 min.

As an O_2 reduction cathode, Pt-black was deposited electrochemically from $K_2[PtCl_6]$ on an FTO (size $5 \text{ cm} \times 5 \text{ cm}$ or $6 \text{ cm} \times 6 \text{ cm}$). Another cathode was composed of stainless steel mesh ($4 \text{ cm} \times 4 \text{ cm}$, or $5 \text{ cm} \times 5 \text{ cm}$, 100 mesh) coated by a thin layer of Nafion (cation exchange resin) and Pt-black was deposited by electrodeposition on the top of the Nafion from $K_2[PtCl_6]$ (designated as SUS-Nf/Pt-black). All the chemicals used in the research are of the commercially available purest grade and used as received.

As for biomass and biowaste samples, a black-colored mixture of pig urine/wash water = 1/4 was obtained from a livestock breeding farmer house in Ibaraki prefecture. Foods slurries in water were prepared by mixing total 100 g of nine kinds of vegetables (spinach, carrot, pimento, cabbage, lettuce, Chinese greens, orange, banana, water melon) and cooked rice (each 10 g) in 1 L water and grinding into fine suspensions as a agricultural and vegetable/food wastes model at home. Blue-green algae, serious pollutants in lakes and rivers, were collected in a small river in Tokyo.

2.2. Cells

The most important point for the enhancement of the high photodecomposition efficiency was the structure of the biophotodecomposition cell (BPCC). A thin layer type cell (Cell 1, Fig. 1a) was used before in order to minimize the solution resistance between TiO_2 photoanode and Pt-coated O_2 -reducing cathode, e.g., the solution layer thickness was usually 5 mm arranged by a spacer made of neoprene rubber between a $5 \text{ cm} \times 5 \text{ cm}$ (or $6 \text{ cm} \times 6 \text{ cm}$) size photoanode and cathode [10]. Stainless steel (SUS) foil charge collectors with 5 mm wide were put on the three edges of the FTO conducting layer both on the anode and the cathode in contact with the spacer, but in Fig. 1, SUS charge collectors are omitted. The highly efficient Cell 2 (Fig. 1b) was fabricated by combining the fundamental Cell 1 structure with a large volume of bulk solution chamber where auto-oxidation of the activated substrate formed on the TiO_2 takes place, realizing very high quantum efficiency. For

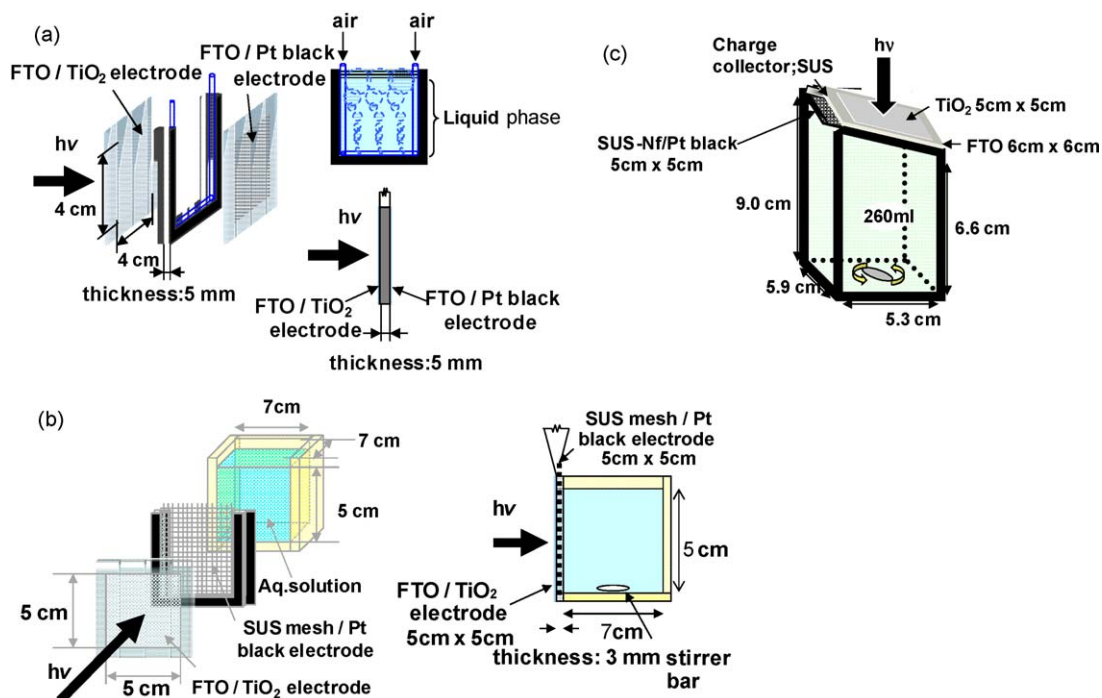


Fig. 1. (a) Thin layer cell (Cell 1). (b) Combined cell (Cell 2) comprising a photoanode/cathode unit and a bulk reactor chamber. (c) Vertical type (Cell 3) for practical use. Charge collectors made of SUS and placed between FTO conducting glass and spacer are not shown in the figures.

this purpose, a Pt-coated SUS mesh (4 cm × 4 cm, 100 mesh) was used as the cathode to assure diffusion of activated substrates into the large chamber. Another vertical type Cell 3 is shown in Fig. 1c for which the photoanode/cathode unit is located on the top of the cell so as to utilize solar irradiation.

2.3. Irradiation and measurements

The UV-A region light intensity was measured by a UV light meter (model UV-340, CUSTOM Co. Ltd.). The TiO₂ film was irradiated at 100 mW cm⁻² white light intensity with a 500 W xenon lamp through an IR-cutoff filter (HA-50), which contained UV-A (290–390 nm) region light with the intensity of 8 mW cm⁻². This UV intensity was the same as that from a solar simulator (PEC-L10 from Peccell Technologies, Inc.) at the irradiance of AM 1.5 G and 100 mW cm⁻². The UV light from a black light was also used at the intensity of 2.5 mW cm⁻² which is weaker than that of the UV light (3.5 mW cm⁻²) under solar irradiation at AM 1.5 and 100 mW cm⁻². As a reference, the UV irradiance on a sunny day of October 28th at 14:50 was 4.5 mW cm⁻² when the total solar irradiance was one sun (100 mW cm⁻²).

The gases (CO₂ and N₂) formed were analyzed by a gas chromatograph (Shimadzu, GC-8A) with a molecular sieve 5A column at 30 °C using argon carrier gas, but CO₂ was analyzed with a silica gel column. For calculating the amount of the total formed CO₂, the gas volume in the gas phase was corrected by its solubility in water. All the photoelectrochemical reactions were performed at 25 °C. NH₄⁺ was analyzed either by an ion chromatograph (Dionex Dx-AQ) by using a cation exchange column (Ion Pac CS12A) with an eluate CH₃SO₃H and an electric conductance detector, or by a DR2800 analyzer from Hach Company, Germany.

3. Results and discussion

3.1. Photodecomposition mechanism and estimation of quantum efficiency for the Cell 1

The reactions in a BPCC composed of a nanoporous semiconductor photoanode and an O₂-reducing cathode for photodecomposition of biomass and its wastes to produce CO₂ and N₂ have been established in our previous papers [8–10]. As known well in a liquid-junction semiconductor photoelectrochemical system [1–3], excitation of electrons from the valence band (VB) to the conduction band (CB) takes place by irradiation of a semiconductor photoanode with the light whose wavelength is shorter than the bandgap of the semiconductor, forming separated electrons (in the CB) and holes (in the VB) (later shown in Eq. (4)), and thus separated charges can induce oxidation and reduction reactions at the photoanode and the cathode, respectively.

One of the merits of the BPCC is that the quantum efficiency of the photodecomposition can be estimated. In conventional semiconductor powder systems, photoelectrochemically separated electrons diffuse to the surface of the semiconductor to reduce O₂ into O₂^{•-} and/or HO₂[•]. To our knowledge it has been difficult to estimate quantum efficiency, and it has not been reported that organic or inorganic compound can be photode-

composed by conventional semiconductor photocatalyst powder systems with a quantum efficiency higher than 1. However, in a photoelectrochemical system using TiO₂ photoanode, so-called current doubling effect has been known, which brings about internal quantum efficiency of 2 (=200%) through one electron injection from the radical produced by oxidation of organic compound by the hole formed on the TiO₂ electrode, as reported, for an example, on the oxidation of 2-propanol [13].

In the BPCC, positive potential is applied from the cathode due to the O₂/H₂O redox couple making the band bending large, which facilitates electron diffusion into the inside of the TiO₂ film bulk and therefore most of the electrons would flow towards cathode via outer circuit. The low charge conducting resistance between particles in the present nanoporous TiO₂ film as reported in the previous papers [8–10] would facilitate this charge transport to the cathode that makes an Ohmic contact with the semiconductor film. Under these circumstances the negative charges passed in the outer circuit could be regarded nearly equal to the amount of the positive charges used effectively for substrate oxidation at the semiconductor. The internal quantum efficiency for the decomposition (= η') could be defined as the ratio of the total decomposition number against photon number effectively used for activating the substrate (Eq. (1)), where the denominator can be regarded nearly equal to the charges passed at the outer circuit in the BPCC.

$$\eta' = \frac{\text{decomposed mol of substrate} \times \text{number of electron involved in one molecular decomposition}}{\text{photon number in mol effectively used for activating the substrate}} \quad (1)$$

It should be noted here that the quantum efficiency in the present paper is expressed by this definition taking 100% to be 1 in accordance with the formal definition in photochemistry field.

The solution volume between photoanode and cathode in the Cell 1 was enlarged by changing the spacer thickness to 1, 5, and 20 mm, the sample solution volume between the electrodes being 2, 8, and 32 mL, respectively. As for a biowaste sample to investigate, livestock wastes especially pig urine are serious pollutants all over the world. The photodecomposition of urea (NH₂)₂-C=O, the main component of urine, was already reported by us using an airtight cylindrical cell producing almost quantitative CO₂/N₂ = 1/1 molar ratio [10]. It should be added that urea is rapidly converted to NH₃ by urease present abundant in urine. A deeply black-colored pig urine mixture with four times of water containing 0.143 M (2570 ppm) NH₄⁺ was used. Since in the thin layer Cell 1 it is difficult to analyze the evolved gaseous products due to the open air cell structure needed to supply O₂ from air, the decomposition of NH₃ was monitored by the decrease of NH₄⁺. It should be added that the pH of the sample solution was 8.3 meaning that almost all the NH₃ is present as NH₄⁺ (pK_a of NH₃ = 9.24). Before this experiment it had been confirmed that disappearance of NH₄⁺ is always accompanied by N₂ formation since the reactivity of intermediates to dinitrogen is very high. The photodecomposition results are shown in Table 1.

Table 1
Photodecomposition of NH₄⁺ in pig urine/water mixture with initial NH₄⁺ of 0.143 M (=2570 ppm) by the Cell 1 in changing the distance (=spacer thickness) between anode and cathode to be 1 mm (2 mL sample solution), 5 mm (8 mL sample solution), and 20 mm (32 mL sample solution) under 8 mW cm⁻² UV irradiation for 18 h.

Spacer thickness (mm)	Soln. vol. (mL)	Decomposition rate in 18 h (%)	Decomposition amount (mmol)	Coulombs corresponding to NH ₃ decomposition (b) (C)	Coulombs passed (a) (C)	η' (=b/a)
1	2	71.0	0.203	62.5	57.0	1.10
5	8	59.4	0.680	181	11.4	15.9
20	32	85.4	3.93	1410	30.1	46.8

By measuring the coulomb number passed in the outer circuit (=activated amount of substrate on TiO_2) and the decomposed amount of NH_3 during 18 h's irradiation, η' values were obtained. The coulombs passed (corresponding to photocurrent) decreased at first from 1 mm spacer cell to 5 mm one, and then increased from 5 mm spacer cell to 20 mm one. The photocurrent is dependent also on the O_2 concentration in the solution as well as on the distance between the electrodes due to the solution resistance. When the liquid thickness becomes thicker from 1 to 5 mm, the increased solution resistance would suppress the photocurrent. However, when the liquid thickness increased from 5 to 20 mm, O_2 from air can be easily dissolved into the solution which would make the photocurrent higher due to the enhanced O_2 concentration at the O_2 -reducing cathode. As a proof for this, air bubbling into the cell with 5 mm spacer enhanced the photocurrent remarkably. In Table 1 the decomposition rate decreased at first and then increased with the solution volume increase, but the total decomposed amount of ammonia increased remarkably by increasing the volume between the electrodes, and that η' value also increased drastically from 1.1 (for 2 mL sample solution) to 15.9 (for 8 mL) and to 46.8 (for 32 mL). It is important here that the total decomposed amount of ammonia increased drastically with the increase of the solution volume. If ammonia was oxidatively decomposed only at the TiO_2 film, such results must have been impossible in the Cell 1. These results exhibit unambiguously that in the bulk solution (dark) oxidative decomposition by O_2 , most probably a kind of auto-oxidative chain reaction of the substrate radicals with O_2 independent of UV light, must have taken place.

3.2. Design of efficient Cell 2

3.2.1. Combination of a thin layer cell unit with a large volume of reaction chamber

In the thin layer Cell 1, it was considered that the enlargement of the cell volume by means of simple enlargement of the electrodes distance between anode and cathode must be unfavorable for the photoelectrochemical process due to the increase of the solution resistance between the electrodes. Therefore, the Cell 2 (Fig. 1b) was designed so as to provide a large bulk solution volume (250 mL) in combination of a BPCC photoreaction center unit (comprising a TiO_2 photoanode and an O_2 -reducing cathode being placed close with each other) at the position facing directly the incident light. A stainless steel mesh coated by both a Nafion polymer thin film and Pt-black was used as the O_2 -reducing cathode such that the activated biomass substrates radicals can diffuse from the TiO_2 nanopores into the large volume of bulk solution through the cathode mesh to undergo dark chain reaction with O_2 there. A 250 mL of black-colored pig urine mixture with four times volume of water whose initial NH_4^+ -N content was 1420 ppm (=0.079 M), was magnetically stirred and irradiated with 100 mW cm^{-2} white light (UV light 8 mW cm^{-2}), then the photodecomposition of the ammonia was investigated by analyzing the decrease of NH_4^+ . During 54 h's UV light irradiation (at 8 mW cm^{-2}), 62.0 C charges were passed which corresponds to activation of 6.43×10^{-4} (=62.0/96500) mol NH_3 by TiO_2 . The NH_3 was decomposed from 1420 ppm

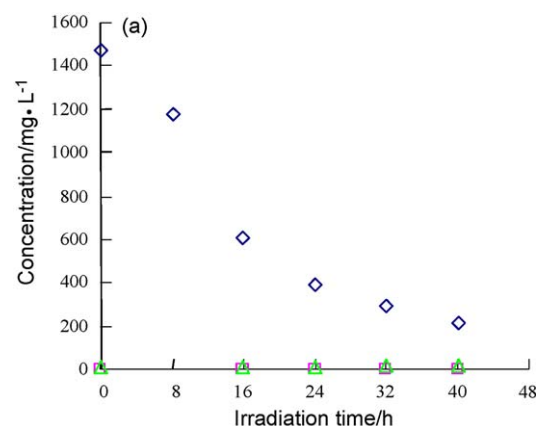


Fig. 2. The changes of NH_4^+ (\diamond), NO_3^- (\triangle) and NO_2^- (\square) with time in the photodecomposition of a 250 mL mixture of pig urine and four times of wash water (NH_4^+ = 1470 ppm, 81.7 M) in the Cell 2 under stirring and 8 mW cm^{-2} UV irradiation.

(=mg L^{-1}) (=20.9 mmol/250 mL) to 120 ppm (=1.8 mmol/250 mL) in 54 h, exhibiting decomposition of 19.1 mmol NH_3 by 3-electron oxidation. Therefore, the obtained η' calculated to be $19.1 \text{ mmol} \times 3 / 0.643 \text{ mmol} = 89.1$ was much higher than that obtained in the Cell 1 mentioned above.

3.2.2. Changes of NH_4^+ , NO_3^- and NO_2^- in pig urine

In the photodecomposition of NH_4^+ in pig urine (NH_4^+ = 1470 ppm, 81.7 mM) in the Cell 2 under stirring and 8 mW cm^{-2} UV irradiation, the changes of NH_4^+ , NO_3^- and NO_2^- with irradiation time are shown in Fig. 2.

After 40 h 85.7% NH_4^+ was decomposed corresponding to decomposition by $5.07 \times 10^3 \text{ C}$, while 72 C passed at the outer circuit during this time, exhibiting η' of $5.07 \times 10^3 \text{ C} / 72 \text{ C} = 70$, also much higher than the values obtained in the Cell 1. In addition to this, it is important in Fig. 2 that NO_3^- and NO_2^- , serious nitrification pollutants, did not increase keeping only a low concentration of ppm level. In conventional oxidative decomposition reactions of NH_3 , N is very often converted to N oxides, causing again environmental pollution and therefore requiring additional denitrification process for cleaning. In the BPCC only one UV irradiation process is sufficient in order to clean biomass wastes.

3.3. Vertical type Cell 3 for solar irradiation

Another type Cell 3 having a vertical cell structure that is more practical for utilizing solar irradiation was fabricated, and photodecomposition of a 60 mM NH_3 aqueous solution (1020 ppm, 260 mL) was investigated by disappearance of NH_4^+ under magnetic stirring and solar simulator irradiation with AM 1.5 and 100 mW cm^{-2} intensity (UV light intensity was 8 mW cm^{-2}), and the results are shown in Table 2 [12]. The decomposition rate increased by stirring and much more by air bubbling, and the η' values were 19.2 without stirring, 83.9 with magnetic stirring, and 116 under both air bubbling and stirring.

Table 2

Photodecomposition of 260 mL ammonia aqueous solution (ca. 60 mM, 1020 ppm) in the vertical type Cell 3 (Fig. 1c, 260 mL) with a solar simulator under AM 1.5 G and 100 mW cm^{-2} intensity (UV-A region 8 mW cm^{-2}) in 6 h [12].

Reaction conditions	Initial NH_3 (mM)	Final NH_3 (mM)	Decomposition rate (%)	Coulombs corresponding to NH_3 decomposition (b) (C)	Coulombs passed (a) (C)	η' (=b/a)
Without stirring	64	60	7.13	342	18.0	19.2
With stirring	60	45	24.9	1123	13.5	83.9
Air bubbling	61	44	27.3	1254	10.8	116

Stirring would be important not only to accelerate the auto-oxidation but also to provide O₂ into the aqueous phase.

3.4. Quantum efficiencies from various aspects

In addition to the internal quantum efficiency η' , external quantum efficiency (η), quantum efficiency of the reaction number based on total incident UV photon number, was obtained by using the IPCE (incident photon to current efficiency) (Eq. (2)). The intrinsic quantum efficiency (η''), quantum efficiency of the reaction number against the UV photon number absorbed by the TiO₂ film, was obtained by measuring the UV photon number absorbed by TiO₂ film (Eq. (3)).

$$\text{External quantum efficiency } \eta = \eta' \times \text{IPCE} \quad (2)$$

intrinsic quantum efficiency η''

$$= \frac{\text{decomposed mol of substrate} \times \text{number of electron involved in one molecular decomposition}}{\text{absorbed photon mol by TiO}_2} \quad (3)$$

The IPCE value for the photodecomposition of the 60 mM NH₃ aqueous solution (Table 2) was 2.5% (=0.025) measured by a monochromatic light of 340 nm. The FTO conducting glass transmitted 40% of the incident UV light, and the absorption by the TiO₂ film was measured to be 88% of the UV light transmitted through the FTO, so that the TiO₂ film alone absorbed 53% (=60 × 88%) of the total incident UV light. Therefore, APCE (=absorbed photon to current efficiency) = IPCE/0.53, so that η'' is represented by $\eta' \times \text{APCE} = \eta' \times (\text{IPCE}/0.53)$. Therefore, when η' was 116, η was calculated to be $116 \times 0.025 = 2.9$, and η'' to be $116 \times 0.025/0.53 = 5.5$. These results demonstrate that the conversion efficiency for the decomposition based on the total incident UV light (η) was nearly 3 (=300%), while the intrinsic quantum efficiency (η'') exceeded 5 (=500%). Quantum efficiency exceeded far over 1 even based on total UV light irradiance.

3.5. Estimation of necessary area of the cells for three examples

In addition to the above fundamental investigations, we have investigated and confirmed that enlargement of BPCC to a submodule with a size of 20 cm × 20 cm electrode area is no problem as will be reported elsewhere. Electrical connection of more than two submodules towards fabricating a larger size module in an electrically parallel or serial way was also no problem. By assuming a 1 m³ (1 m × 1 m × 1 m) module composed of 25 pieces of anode/cathode with the size of 20 cm × 20 cm, following estimations were conducted based on actual decomposition data of pollutants conducted by using the laboratory scale Cell 2. It should be noted here that it is not needed to entirely photodecompose the pollutants under solar irradiation in 1 day. Even if it is necessary to irradiate for more than 1 day, it suffices if enough volume capacity of modules was used depending on the solar irradiation time needed. The following examples estimated based on the present BPCC have been impossible to conduct by conventional photocatalyst powder systems.

3.5.1. Pig urine example

From photodecomposition data of black-colored pig urine/wash water = 1/4 mixture, necessary area for applying modules for solar decomposing the wastes was estimated. The Cell 2 (250 mL) was used for photodecomposition of the wastes (NH₄⁺ = 1470 ppm) with 8 mW cm⁻² UV irradiation, resulting in 85.7% decomposition of NH₄⁺ after 40 h. After the 40 h, BOD (mg L⁻¹) was decreased from 1360 to 53 ppm (96.1% decrease) and solid suspension (SS, mg L⁻¹) from 5000 to 787 ppm (84.7% decrease). It should be noted

that even solid suspensions (mainly biomass wastes) decreased under irradiation. It is inferred that intermediate radicals attack the solid inducing decomposition into soluble states and then further into N₂ and CO₂. It is now estimated that 50 h is sufficient to clean this urine/water mixture by solar irradiation. It is assumed that the decomposition is proportional to the UV photon density, and that average 3 mW cm⁻² solar UV irradiance is present for 7 h in 1 day. Since one pig issues average about 3 L urine in 1 day amounting to 15 L mixture of urine/four times wash water, one pig needs about 286 L [=15 L × (50/7) × (8/3)] module reaction volume for satisfied cleaning. It is then calculated that 1 m³ module (1 m × 1 m × 1 m) can treat 3.5 pigs' urine for solar decomposition/cleaning on the above assumptions. It means for instance that around 300 m² area (=30 m × 10 m) is sufficient for 1000 pigs by using 1 m³ (=1 × 1 × 1 m) modules. This much area would be only about 10–20% area of a pig breeding house, reasonable area for solar cleaning of pig's urine.

3.5.2. Slurry suspensions of food mixture in water

Another estimation example of cleaning food wastes at houses: Fine suspensions of nine kinds of vegetables and cooked rice in water (100 g L⁻¹) was prepared by a mixer, photodecomposed in a 250 mL Cell 2 under UV light of 2.6 mW cm⁻² which is weaker than the one sun solar UV irradiance (3.5 mW cm⁻²), and the photodecomposition (into CO₂ and N₂, refer [8] as products investigated by model compounds) was monitored by weight loss of the foods after drying a portion of sampled mixture. After sampling out the suspended solution, slurry/water was evaporated without any filtration and the mixture was dried completely, so that almost all the soluble components were measured also as residual materials. The weight loss was almost linear with time (Fig. 3), and after 250 h's irradiation 70% weight was lost, exhibiting that 70% of the food mixture was photodecomposed into gaseous products (mainly CO₂ and N₂), water, and other volatile low molecular compounds during 250 h.

We have already published that even cellulose and lignin were photodecomposed in the BPCC [9], lignin was photodecomposed 100% as confirmed by the CO₂ formed [9], and even suspended cellulose was photodecomposed as confirmed by the photoreaction of used paper [10]. As later shown in Fig. 4 in the photodecomposition of solid state blue-green algae, the solid suspension disappeared almost completely in the photodecomposition after 453 h. However, in the present experiment for the food mixture, we stopped the experiment at the weight loss of 70%.

By a simple estimation 100% weight loss could be achieved in 360 h. Since average 200 g (wet-based) vegetable/foods garbage is issued per person in 1 day, 8 L/day water suspension should be treated in (360/7=) 51 days for a family with four persons (totally 800 g/day). Therefore (8 L × 51) = 410 L volume modules are

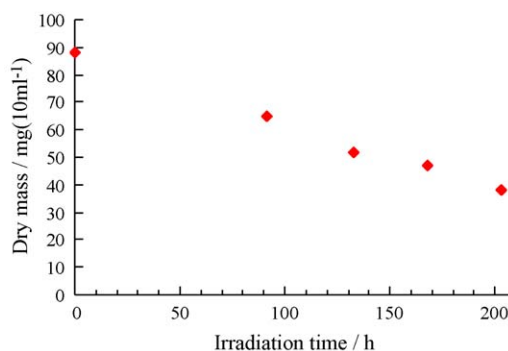


Fig. 3. Photodecomposition of vegetables/food mixture slurry in water as studied by weight loss after sampling and drying for each photoreaction time. Irradiation with UV light at 2.5 mW cm⁻².

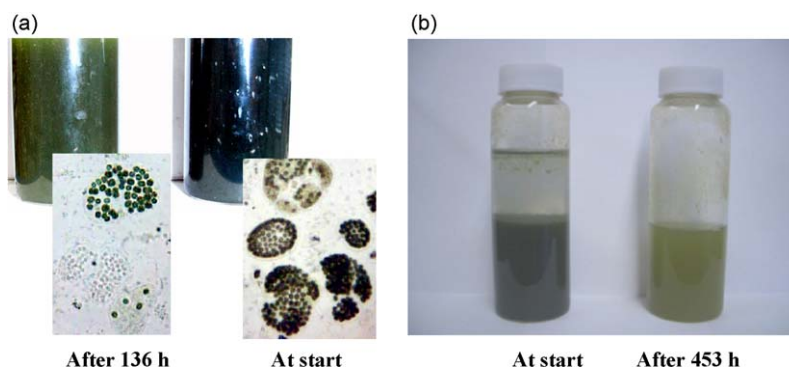


Fig. 4. Photodecomposition of blue-green algae under 100 mW cm^{-2} xenon lamp irradiation (UV 8 mW cm^{-2}): (a) After 136 h irradiation the contents of the cells nearly degraded, and (b) after 453 h the algae almost disappeared.

needed in this case, i.e., about 0.5 m^3 module would be sufficient to totally decompose such garbage by solar irradiation. It should be added that the module has to be divided into at least 51 pieces submodules, each having 8 L capacity.

3.5.3. Blue-green algae

Blue-green algae, serious pollutants in lakes and rivers, was photodecomposed with white light of 100 mW cm^{-2} (8 mW cm^{-2} UV intensity) in the thin layer Cell 1 (64 mL, the electrodes distance being 4 cm). The I – V characteristics are shown in Fig. 5 that are the results by the cells with 5 mm spacer (8 mL volume) and 4 cm spacer (64 mL volume). A long term photodecomposition was conducted by the latter 64 mL cell. The contents of the algae cells almost disappeared in 136 h (Fig. 4a, picture of a microscope of 400 magnifications) and the solid algae almost disappeared in 453 h (Fig. 4b). It should be noted that the algae should also grow during this experiment since white light was irradiated, but the photodecomposition was much faster than the growth.

At present the main objective of the present BPCC is solar decomposition and cleaning of pollutants, but in the case of Fig. 4, 1 m^2 module can generate 0.28 W electrical power as estimated from the laboratory scale cell, so that 10 m^2 module(s) can generate 2.8 W in solar decomposition of the green-blue algae. By a rough estimation, this much area module could supply energy to an LED lamp composed of $0.2 \text{ W} \times 7$ pieces LED for crime prevention in the night for 14 h if the electrical power is stored in a secondary battery in the day time.

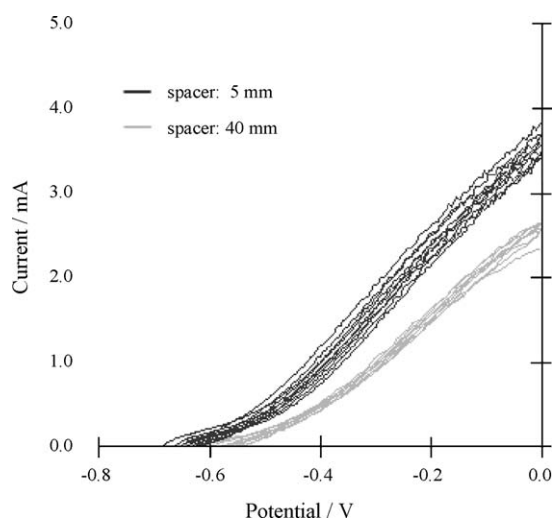
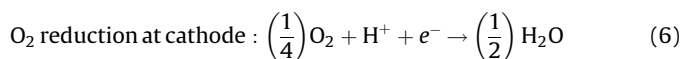


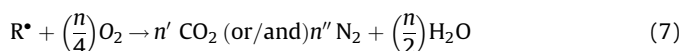
Fig. 5. I – V characteristics of blue-green algae in the Cell 1 with a 5 mm spacer (cell volume 8 mL), and a 40 mm spacer (cell volume 64 mL). Both the I – V curves decreased on repeated scanning.

3.6. Photodecomposition mechanism

The mechanism of the present UV light-activated decomposition of biomass and organic compounds by the biophotochemical cell is shown in Fig. 6. The reactions are represented by the Eqs. (4)–(7) when the substrate is RH and the semiconductor (SC).



Chain auto-oxidation of R^* in the bulk (between anode and cathode for the Cell 1, and in the auto-oxidation chamber for the Cell 2):



where n , n' and n'' depend on the R structure.

In the present paper it is important that the activated substrate (R^*) undergoes dark auto-oxidation by the bulk O_2 as a major decomposition reaction to CO_2 or/and to N_2 whose internal quantum efficiency can exceed 100 (=10000%). This auto-oxidation must take place by a chain reaction between R^* and O_2 , and is regarded as a kind of combustion of fuels in a gas phase for which activation is ignition of the fuel by fire. In the present BPCC,

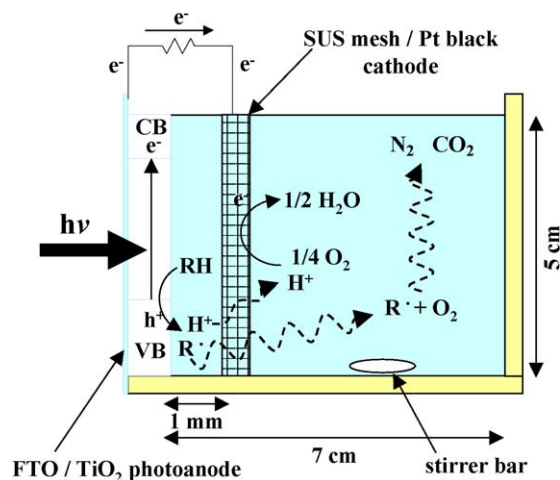


Fig. 6. Photodecomposition mechanism of biomass wastes in BPCC comprising activation of the substrates by UV light at the photoanode/cathode unit and auto-oxidation of the activated substrates by O_2 in bulk solution.

activation by UV light is like an ignition by fire, and the auto-oxidation of the activated organic compounds can be regarded as a kind of combustion. In this sense the fundamental Cell 1 structure composed of photoanode/O₂-reducing cathode unit placed in a close position could be called “a photonic igniter”. The detailed mechanism of the auto-oxidation depends on the kind of R, and should be the subject open to future researches.

3.7. Summarized characteristics of the BPCC (biophotochemical cell)

The characteristics of the BPCC are summarized and discussed as follows in comparison to conventional semiconductor powder systems.

- (1) It is easy and not a problem to separate the wastes solution or suspension from the semiconductor film after the decomposition in a BPCC allowing also sample circulation systems. However, for conventional semiconductor powder systems the semiconductors need usually to be loaded on some carrier for separation purpose after use, which brings about serious drawbacks that the carrier material prohibits UV light absorption by the semiconductor and also reduces active semiconductor surface area, which decreased their activity drastically in comparison to the present BPCC.
- (2) To discuss more details about the above item (1); in conventional semiconductor fine powder systems, UV light is always irradiated on the semiconductors through liquid phase. Especially when the pollutant concentrations and volumes are high, irradiation on semiconductors is strongly inhibited due to the light absorption by carrier materials (of the semiconductors) and by the solutes in wastes liquid (usually water), making their activity very weak. While in the BPCC the semiconductor thin film photoanode is exposed directly to the incident light, the hindrance of light absorption by concentrated solutes, even suspension and colored compounds are nearly negligible to allow sufficient irradiation of the semiconductor. Strongly colored compounds such as livestock wastes or Coca-Cola [10] could also be photodecomposed by a BPCC without any problem. For a comparison, if UV light is irradiated on conventional semiconductor powders through wastes in water of 1 mm thickness containing 1 mM solutes that absorb UV region light with the extinction coefficient ϵ of $10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$, only 10% UV light can reach the semiconductor based on the Lambert–Beer equation, $\text{absorbance} = -\log(I_0/I) = \epsilon c \ell = 1$, where I_0 is the incident light on the water, I light intensity passed through the liquid phase of ℓ cm thickness, and c concentration of the solutes/M. On the contrary, when taking as an example a BPCC with 10 μm porous semiconductor film thickness, and assuming that (1) the average liquid phase fraction in the porous film is 1/3, and (2) the average reaction position in the film is at 3 μm depth along the incident light direction, when the solutes concentration is 1 mM, the absorbance by the liquid is only 0.001 ($=10^4 \times 10^{-3} \times (3 \times 10^{-4}) \times 1/3$) showing that the light absorption by the liquid is entirely negligible, demonstrating also that three orders of more concentrated pollutants (1 M) can receive the same UV irradiation as the 1 mM pollutants for conventional powder systems.
- (3) By utilizing the BPCC it was for the first time proved that photodecomposition of biomass wastes by semiconductors can proceed with internal quantum efficiency over 80, which has allowed highly efficient cell design enabling dark auto-oxidation and decomposition in a large volume chamber, leading to cleaning of a highly concentrated (higher than 10^5 ppm) and a large scale of wastes solution or solid suspension by solar irradiation. These are entirely different

from conventional so-called powder-based photocatalysts that can usually treat only a low concentration solution (<100 ppm order) and a smaller volume of pollutants solution.

- (4) One of the important points of a BPCC is that solid suspension in water can also be easily photodecomposed. Activated pollutant radicals in solution would attack and decompose the suspended or coexisted biomass solids into solubilized form and finally into CO₂ and N₂. However, for powder-based or carrier-loaded semiconductors, such has been impossible due to the serious inhibition of UV light irradiation on semiconductors by the suspended solids.
- (5) Since CO₂ and N₂ are the sole products of carbon and nitrogen, respectively, with additional formation of H₂O by the BPCC [8–10], the system is entirely compatible with the material circulation in nature, different from other cleaning methods used now that often cause secondary pollution problems.
- (6) At the present stage the BPCC is used mainly for environmental cleaning by solar irradiation, while the simultaneously generated electrical power is not large, but in the near future, the BPCC has a potential for generating larger scale electrical power by utilizing the large amount of biomass wastes (about 130 EJ/y, world) [14] amounting to nearly 1/3 of the world energy demand in a year (450 EJ/y, world, at present).
- (7) Finally it should be added shortly about the durability of the TiO₂ film. Durability of the TiO₂ film is an important point for practical use, but its durability study is the research objective for future. We can say within the scope of the present paper that the TiO₂ film can be used at least for 453 h's irradiation without any problem as shown in the experiment of Fig. 4. It would be of importance to add that, when the film lost its activity, irradiation of the film under air by the same light recovered its activity almost to the initial one.

4. Conclusions

UV light-activated decomposition/cleaning of high concentration ($>10^3$ – 10^4 ppm) biomass, its wastes and organic compounds involving also solid suspensions into CO₂ and N₂ was achieved by using a specially designed biophotochemical cell (BPCC) composed of a photoanode/cathode unit and a large auto-oxidation chamber. The Cells 2 and 3 were especially efficient giving a high internal quantum efficiency of over 80 (=8000%) for pig urine. The required area for solar decomposition/cleaning of biomass wastes was estimated taking as examples pig urine, food samples mixture, and blue-green algae, demonstrating promising systems for near future environmental solar cleaning.

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